

Supporting Information

Theoretical Understanding of Potential-Dependent Electrocatalytic CO₂RR and Competition with HER upon Cobalt Single Atom Supported by Phthalocyanine Monolayer

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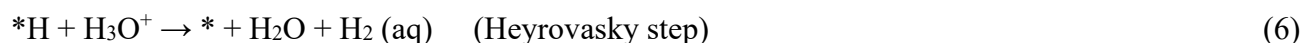
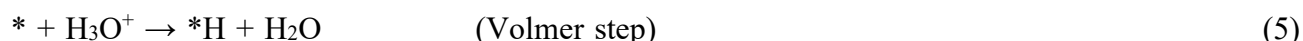
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Note 1. Reaction Energy calculation

There are four elementary reactions in CO₂RR from CO₂ to CO, including CO₂ chemisorption, two protonation steps, and CO desorption.



There are two elementary reactions in HER:



Where * refers to the Co-PC slab, *CO₂, *COOH, *CO, and *H are intermediates adsorbed on catalyst slab. In constant potential model based on GC-DFT, the amount of charge of the system is not constant, and the amount of electron transfer of elementary reactions is not integer necessarily. It should also be noted that the slab and adsorbed intermediates are not electrically neutral except at U_{PZC} .

The reaction energies were calculated using following equations:

$$\Delta\Omega (1) = \Omega (*\text{CO}_2) - \Omega (*) - \Omega (\text{CO}_2(\text{aq})) + RT \ln \frac{c^\ominus}{c_{\text{CO}_2(\text{aq})}}$$

$$\Delta\Omega (2) = \Omega (*\text{COOH}) + \Omega (\text{H}_2\text{O}) - \Omega (*\text{CO}_2) - \Omega (\text{H}_3\text{O}^+) + 0.0592\text{pH}$$

$$\Delta\Omega (3) = \Omega (*\text{CO}) + 2\Omega (\text{H}_2\text{O}) - \Omega (*\text{COOH}) - \Omega (\text{H}_3\text{O}^+) + 0.0592\text{pH}$$

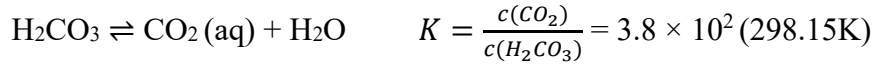
$$\Delta\Omega (4) = \Omega (*) + \Omega (\text{CO}(\text{aq})) - \Omega (*\text{CO}) + RT \ln \frac{c_{\text{CO}(\text{aq})}}{c^\ominus}$$

$$\Delta\Omega (5) = \Omega(*\text{H}) + \Omega (\text{H}_2\text{O}) - \Omega (*) - \Omega (\text{H}_3\text{O}^+) + 0.0592\text{pH}$$

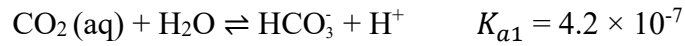
$$\Delta\Omega (6) = \Omega (*) + \Omega (\text{H}_2\text{O}) + \Omega (\text{H}_2(\text{aq})) - \Omega (*\text{H}) - \Omega (\text{H}_3\text{O}^+) + 0.0592\text{pH} + RT \ln \frac{c_{\text{H}_2(\text{aq})}}{c^\ominus}$$

We considered the effect of the concentration of soluble species on $\Delta\Omega$ (eV). For the protonation steps of CO_2RR and HER , the effect of pH on $\Delta\Omega$ is 0.0592pH. For (1), (4), and (6) reaction, the contribution of saturated concentration of $\text{CO}_2(\text{aq})$, $\text{CO}(\text{aq})$, and $\text{H}_2(\text{aq})$ on $\Delta\Omega$ are $RT \ln \frac{c^\ominus}{c_{\text{CO}_2(\text{aq})}}$, $RT \ln \frac{c_{\text{CO}(\text{aq})}}{c^\ominus}$, and $RT \ln \frac{c_{\text{H}_2(\text{aq})}}{c^\ominus}$, respectively.

Under $P=1$ atm, $T=298.15\text{K}$, $c_{\text{CO}(\text{aq})}=8.9 \times 10^{-4}$ mol/L, $c_{\text{H}_2(\text{aq})}=7.7 \times 10^{-4}$ mol/L. The concentration of CO_2 is greatly affected by pH; in electrolyte solution, the following chemical equilibria exists between H_2CO_3 and CO_2 :



According to the K value, $\text{CO}_2(\text{aq})$ is the predominant form, accounting for more than 99.7%, and H_2CO_3 is less than 0.3%. So, we only considered the $\text{CO}_2(\text{aq})$. There are two proton dissociation steps for $\text{CO}_2(\text{aq})$:



We can calculate the concentration distribution fraction of species at different pH:

$$\delta_2 = \frac{c^2(\text{H}^+)}{c^2(\text{H}^+) + c(\text{H}^+)K_{a1} + K_{a1}K_{a2}}$$

$$\delta_1 = \frac{c(\text{H}^+)K_{a1}}{c^2(\text{H}^+) + c(\text{H}^+)K_{a1} + K_{a1}K_{a2}}$$

$$\delta_0 = \frac{c(\text{H}^+)K_{a1}}{c^2(\text{H}^+) + c(\text{H}^+)K_{a1} + K_{a1}K_{a2}}$$

δ_2 , δ_1 , δ_0 represent the concentration distribution fraction of $\text{CO}_2(\text{aq})$, HCO_3^- and CO_3^{2-} respectively¹.

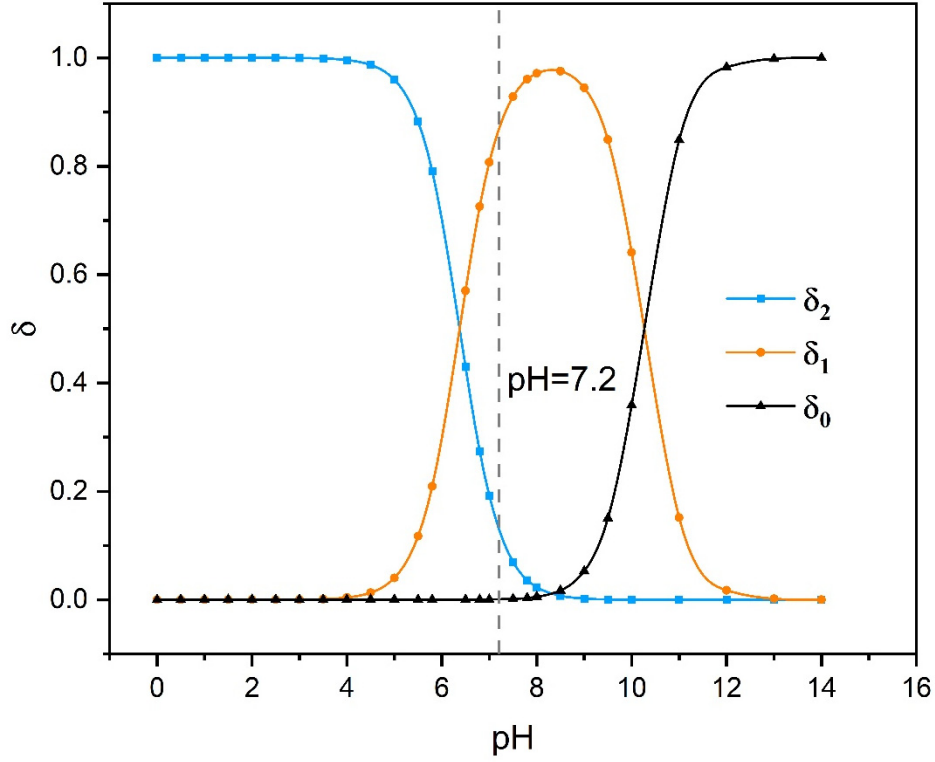


Figure S1. The distribution fraction of $\text{CO}_2(\text{aq})$, HCO_3^- and CO_3^{2-} at different pH

In 0.5 M KHCO_3 solution, at $\text{pH} = 7.2$, $c_{\text{CO}_2(\text{aq})} = c_{\text{sum}} \times \delta_2 = 0.5 \times 0.13 = 0.065 \text{ mol/L}$. So we can get the contribution of $\text{CO}_2(\text{aq})$, $\text{CO}(\text{aq})$ and $\text{H}_2(\text{aq})$ concentration on $\Delta\Omega$, as:

$$\Delta\Omega(\text{CO}_2) = RT \ln \frac{c^\ominus}{c_{\text{CO}_2(\text{aq})}} = 0.07 \text{ eV}$$

$$\Delta\Omega(\text{CO}) = RT \ln \frac{c_{\text{CO}(\text{aq})}}{c^\ominus} = -0.18 \text{ eV}$$

$$\Delta\Omega(\text{H}_2) = RT \ln \frac{c_{\text{H}_2(\text{aq})}}{c^\ominus} = -0.184 \text{ eV}$$

Note 2. The adsorption configuration

We respectively consider two adsorption configurations for $\ast\text{CO}_2$ and $\ast\text{COOH}$.

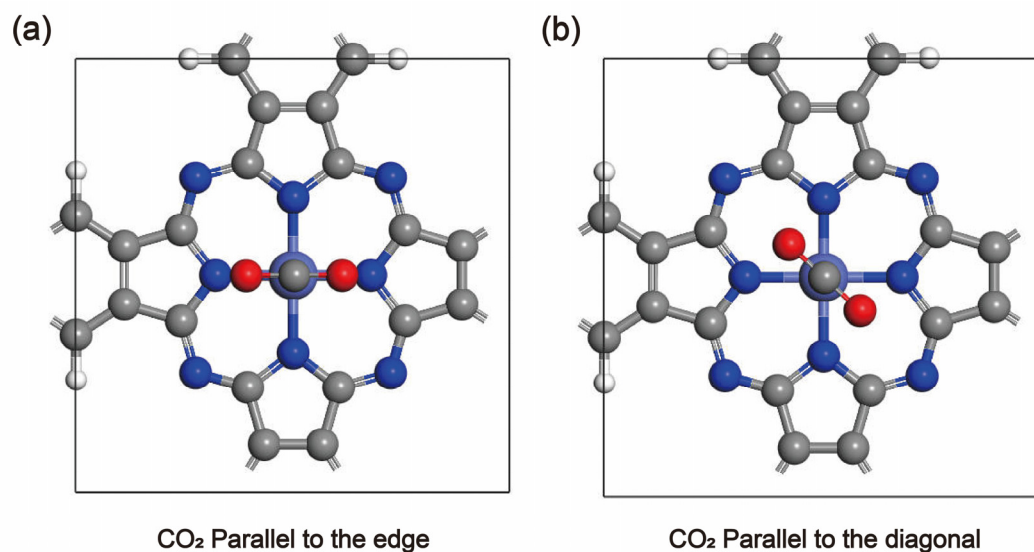


Figure S2. Two adsorption configurations for $\ast\text{CO}_2$

Table S1. The grand canonical energy (Ω) of two adsorption configurations for chemical adsorption of CO₂

U vs. SHE	-0.8 V	-1 V	-1.2 V
$\Omega(\text{a})$ /Ha	-362.0154	-363.1789	-364.3459
$\Omega(\text{b})$ /Ha	-362.0175	-363.1812	-364.3482
$\Omega(\text{a}) - \Omega(\text{b})$ /eV	0.059	0.062	0.065

Table S2. The grand canonical energy (Ω) of two adsorption configurations for physical adsorption of CO₂

U vs. SHE	-0.8 V	-1 V	-1.2 V
$\Omega(\text{a})$ /Ha	-362.0167	-363.1780	-364.3397
$\Omega(\text{b})$ /Ha	-362.0169	-363.1782	-364.3399
$\Omega(\text{a}) - \Omega(\text{b})$ /eV	0.0042	0.0044	0.0046

The (b) configuration is more stable than the (a) configuration for physical and chemical adsorption of CO₂. So, all subsequent GC-DFT calculations only considered (b) configuration.

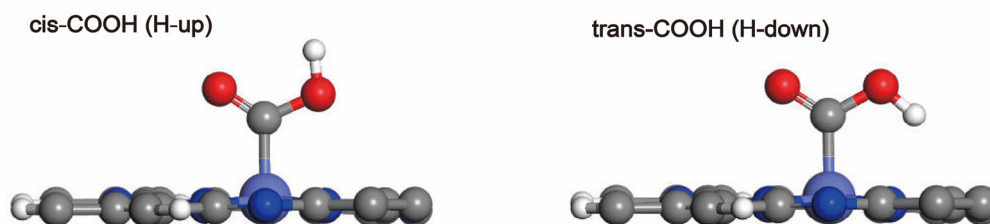


Figure S3. Two adsorption configurations for *COOH

Table S3. The grand canonical energy Ω of two adsorption configurations of *COOH

U vs. SHE	-0.8 V	-1 V	-1.2 V
Ω (up) /Ha	-362.4556	-363.6220	-364.7918
Ω (down) /Ha	-362.4543	-363.6219	-364.7926
$\Omega(\text{up}) - \Omega(\text{down})$ /eV	-0.034	-0.003	0.0195

The grand canonical energy (Ω) of cis-COOH and trans-COOH is very close, and there is no consistent trend in the comparison of Ω . To save computing costs, we only consider trans-COOH. It should be noted that trans-COOH molecule is parallel to the slab diagonal because of the calculation result of adsorption configurations for *CO₂ above.

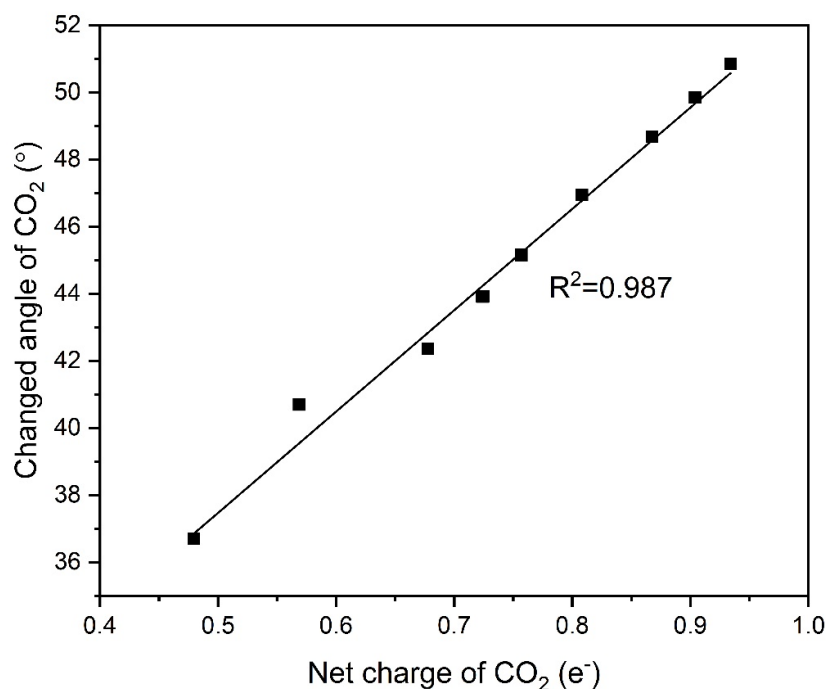


Figure S4. Linear correlation between net charge and changed angle of CO₂ in CO₂ chemisorption.

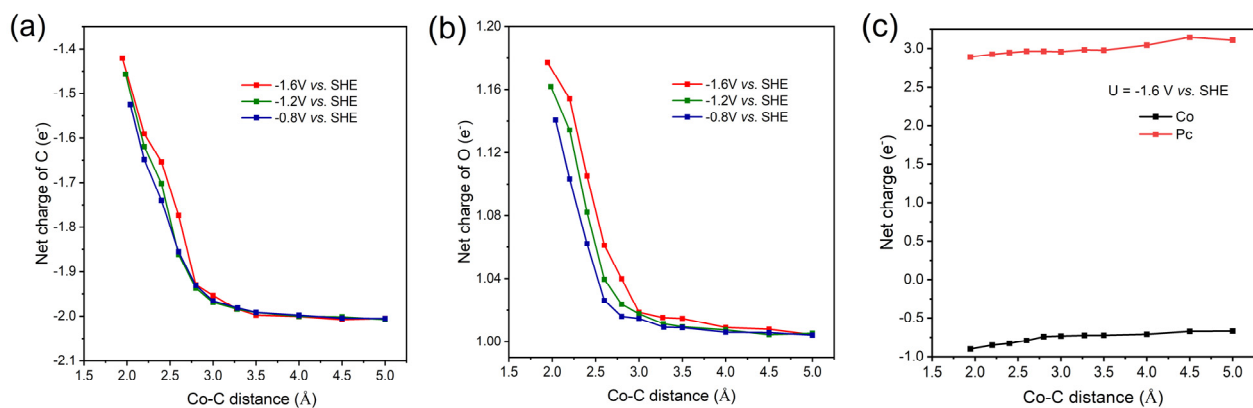


Figure S5. Evolution of Bader charge on (a) O atom, (b) C atom, (c) Co atom and Pc support

Note 3. The vibrational contribution

Calculating the frequencies of all atoms of system is expensive. To reduce computational consumption, we fixed the slab and only calculated the frequencies of adsorbed molecules and free molecules. For internal energy correction $\Delta \int_0^{298.15K} C_v dT$, we ignored the translational energy contribution and rational energy contribution, only considered primary vibrational energy contribution. E_{ZPE} and TS can also be obtained in vibrational calculation. We named the contribution $E_{ZPE} + \Delta \int_0^{298.15K} C_v dT - TS$ on Helmholtz free energy as A_{vib} .

Table S4. A_{vib} (eV) contribution on $\Delta\Omega$ of element reactions at different applied potential

U vs. SHE Reactions	0.2 V	0 V	-0.2 V	-0.4 V	-0.6 V	-0.8 V	-1.0 V	-1.1 V	-1.2 V	-1.3 V	-1.4 V	-1.5 V	-1.6 V
CO ₂ physisorption	-0.0239	-0.0262	-0.0215	-0.0248	-0.0246	-0.0260	-0.0244	-0.0232	-0.0251	-0.0248	-0.0255	-0.0236	-0.0257
(1)	-0.0361	-0.0711	-0.0730	-0.0419	-0.0434	-0.0616	-0.0646	-0.0426	-0.0792	-0.0714	-0.0921	-0.0867	-0.0599
(2)	-	-	-	0.0141	-0.0249	-0.0201	-0.0156	-	0.0180	-	0.0094	-	-0.0292
(3)	-	-	-	-0.2111	-0.0962	-0.1548	-0.1550	-	-0.1894	-	-0.0981	-	-0.1022
(4)	-	-	-	0.0285	0.1016	0.0733	0.0579	-	0.0454	-	0.1316	-	0.0905
(5)	-	-	-	-0.1296	-0.1180	-0.1431	-0.1373	-0.1372	-0.1419	-0.1342	-0.1447	-0.1379	-0.1358
(6)	-	-	-	-0.2607	-0.2709	-0.2844	-0.2739	-	-0.2706	-	-0.2786	-	-0.2674

Note 4. The proton donors at different pH

In protonation of CO₂RR and HER, the proton donors could be H₃O⁺ or H₂O.

Two protonation steps of CO₂RR are:



Two protonation steps of HER are:



Take *CO₂ protonation as an example:

$$\Delta\Omega (*\text{CO}_2 + \text{H}_3\text{O}^+ \rightarrow *\text{COOH} + \text{H}_2\text{O}) = \Omega (*\text{COOH}) + \Omega (\text{H}_2\text{O}) - \Omega (*\text{CO}_2) - \Omega (\text{H}_3\text{O}^+) + 0.0592\text{pH}$$

$$\Delta\Omega (*\text{CO}_2 + \text{H}_2\text{O} \rightarrow *\text{COOH} + \text{OH}^-) = \Omega (*\text{COOH}) + \Omega (\text{OH}^-) - \Omega (*\text{CO}_2) - \Omega (\text{H}_2\text{O}) - 0.0592 \times (14 - \text{pH})$$

$$\Delta\Omega (\text{difference}) = \Delta\Omega (*\text{CO}_2 + \text{H}_3\text{O}^+ \rightarrow *\text{COOH} + \text{H}_2\text{O}) - \Delta\Omega (*\text{CO}_2 + \text{H}_2\text{O} \rightarrow *\text{COOH} + \text{OH}^-) = [2\Omega (\text{H}_2\text{O}) - \Omega (\text{H}_3\text{O}^+) - \Omega (\text{OH}^-) + 0.8288] \text{ eV}$$

It is can be found that $\Delta\Omega$ (difference) is independent on pH, and also $\Delta\Omega$ (difference) of all element reactions are the same because the Ω of each intermediate is offset in the calculation. We calculated the $\Delta\Omega$ (difference) at different applied potentials (Table S7). The value of $\Delta\Omega$ (difference) is always less than 0, which indicates that, for all protonation steps, H₃O⁺ being as proton donors is more favourable than H₂O at any pH and potential.

Table S5. $\Delta\Omega$ (difference) at different potential

<i>U</i> vs. SHE	-0.4 V	-0.6 V	-0.8 V	-1.0 V	-1.2 V	-1.4 V	-1.6 V
$\Delta\Omega$ (difference) /eV	-0.4753	-0.4751	-0.4979	-0.4931	-0.4946	-0.5040	-0.4835

Note 5. CO desorption

CO in adsorbed state and in electrolyte solution keep an desorption equilibrium, $^*CO \rightleftharpoons ^* + CO(aq)$.

$$\Delta\Omega(des) = \Delta\Omega^\theta(des) + RT \ln \frac{P_{CO(aq)}}{P^\theta} \text{ (or } RT \ln \frac{c_{CO(aq)}}{c^\theta} \text{)}$$

Meanwhile, CO in bulk and in gas phase keep a solubility equilibrium, $CO(aq) \rightleftharpoons CO(g)$.

$$\Delta\Omega(sol) = \Delta\Omega^\theta(sol) + RT \ln \frac{P_{CO(g)}}{P_{CO(aq)}}$$

The value of $\Delta\Omega^\theta(des)$ is equal to the opposite number of the grand canonical adsorption energy of CO. When $\Delta\Omega(des)$ is less than or equal to 0, CO will spontaneously desorption from the catalysts surface. Similarly, when $\Delta\Omega(sol)$ less than or equal to 0, CO gas will separate out from solution. In general, we cannot change the value of $\Delta\Omega^\theta(sol)$ but we can change the value of $\Delta\Omega^\theta(des)$ by selecting different catalysts. More positive $\Delta\Omega^\theta(des)$ means stronger adsorption between catalysts and CO. Too strong adsorption will lead to CO remain on the surface sufficiently long to poison the active site or possibly undergo further conversion to hydrocarbon products, and makes $P_{CO(aq)}$ smaller. In solubility equilibrium, smaller $P_{CO(aq)}$ will adverse to CO gas separate out from bulk electrolyte. On the contrary, more negative $\Delta\Omega(des)$ will lead to $P_{CO(aq)}$ larger, which beneficial to CO gas separating.

The low solubility for CO in water, 0.89 mM at $T = 298.15K$, $P = 1atm$, contributed to $\Delta\Omega(des)$ about -0.18 eV according to Chemical reaction isotherm. when $\Delta\Omega^\theta(des)$ is greater than 0.18 eV for one catalyst, CO (aq) will not maintain a saturated concentration instead of a smaller concentration to enable CO to desorb from catalyst surface (Figure S6).

When CO desorption just occur to be spontaneous:

$$\Delta\Omega(des) = \Delta\Omega^\theta(des) + RT \ln \frac{c_{CO(aq)}}{c^\theta} = 0$$

$$-RT \ln \frac{c_{CO(aq)}}{c^\theta} = \Delta\Omega^\theta(des)$$

$$c_{CO(aq)} = e^{\frac{-\Delta\Omega^\theta(des)}{RT}}$$

For example, $\Delta\Omega^\theta(des)$ for Fe-Pc is about 1.18 eV at -1.0 V vs. SHE. To enable CO desorption is spontaneous, the CO (aq) should be less than 1.129×10^{-17} mmol/L theoretically. This value is too small, but this is only true for static solutions. Fe-Pc has bad catalytic activity of CO₂RR in experiments², it is because of its strong adsorption with CO.

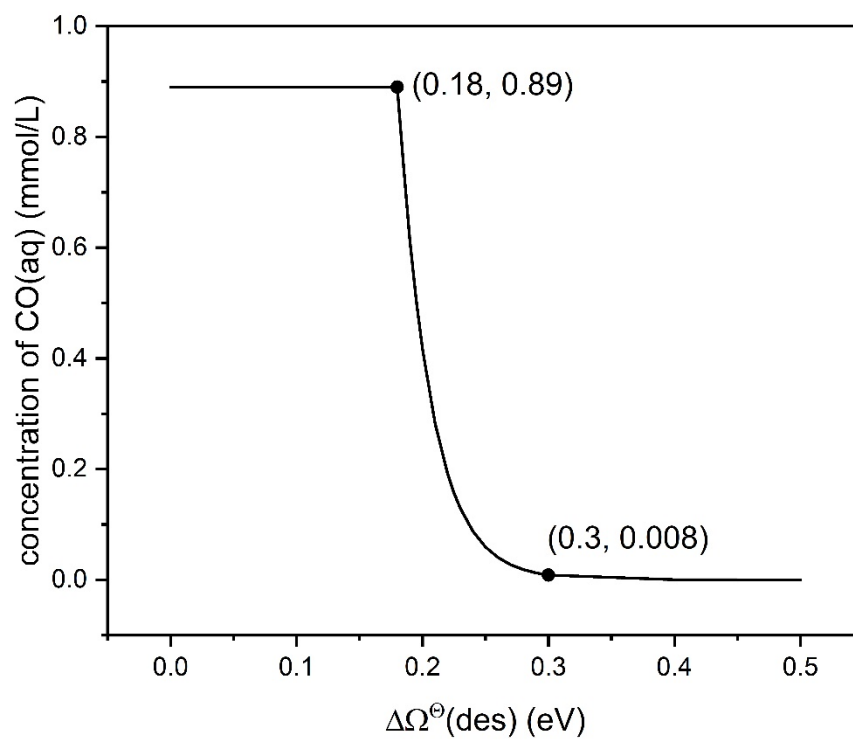
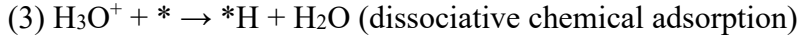
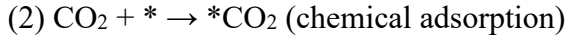
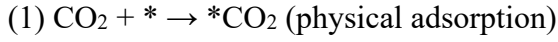


Figure S6. The relation between CO concentration in electrolyte solution and $\Delta\Omega(\text{des})$ of catalysts.

Note 6. The coverage competition of active sites

We only considered the first step that competes for active sites of CO₂RR and HER, and ignored the other adsorbed species.



When these competitive reactions reach the state of the thermodynamic equilibrium, by Langmuir equation:

$$k_{ads,i} (1 - \theta_{\text{CO}_2(\text{phy})} - \theta_{\text{CO}_2(\text{che})} - \theta_H) = k_{des,i} \theta_i$$
$$K_i = e^{\frac{-\Delta\Omega_i}{RT}} = \frac{k_{ads,i}}{k_{des,i}}$$

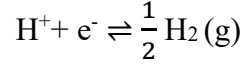
We can derive that:

$$\theta_i = \frac{K_i}{1 + K_{\text{CO}_2(\text{phy})} + K_{\text{CO}_2(\text{che})} + K_H}$$
$$\theta_* = \frac{1}{1 + K_{\text{CO}_2(\text{phy})} + K_{\text{CO}_2(\text{che})} + K_H}$$

i represents adsorbates including physically adsorbed CO₂, chemically adsorbed CO₂, and adsorbed H. k_{ads} , k_{des} , θ and K represent the speed constant of adsorption and desorption, degree of coverage and equilibrium constant, respectively.

Note 7. DFT calculations based on CHE model

As a comparison, the CHE model was also employed to simulate CO₂RR and HER. When the 1 bar of gas H₂ is in equilibrium with the pair of proton and electron at pH = 0, 0 V vs. SHE is defined. In this method, the chemical potential of H⁺ + e⁻ is equal to the $\frac{1}{2}$ H₂ at U = 0 V vs. SHE^{3,4}.



When $U = 0$ V, $\mu(\text{H}^+) + \mu(\text{e}^-) = \frac{1}{2} \mu(\text{H}_2)$

When $U \neq 0$ V, $\mu(\text{H}^+) + \mu(\text{e}^-) = \frac{1}{2} \mu(\text{H}_2) - |eU|$.

In CHE model, Gibbs free energy G is as thermodynamic property of energy.

$$G = E_{DFT} + E_{ZPE} + \Delta \int_0^{298.15K} C_p dT - T\Delta S$$

Where E_{DFT} , E_{ZPE} , $\Delta \int_0^{298.15K} C_p dT$, T and S represent electronic total energy of the system, zero-point energy, enthalpy energy correction, temperature and entropy respectively.

There are four elementary reactions in CO₂RR:



There are two elementary reactions in HER:



The amount of charge transfer of all elementary reactions is constant, and equal to the amount of the proton coupling, no matter catalysts and applied potential. All adsorbed intermediates are electroneutral.

$$\Delta G (7) = G (*\text{CO}_2) - G (\text{CO}_2) - G (*)$$

$$\Delta G (8) = G (*\text{COOH}) - G (*\text{CO}_2) - 0.5G (\text{H}_2) + 0.0592\text{pH}$$

$$\Delta G (9) = G (*\text{CO}) + G (\text{H}_2\text{O}) - G (\text{COOH}) - 0.5G (\text{H}_2) + 0.0592\text{pH}$$

$$\Delta G (10) = G (*) + G (\text{CO}) - G (*\text{CO})$$

$$\Delta G (11) = G (*\text{H}) - G (*) - 0.5G (\text{H}_2) + 0.0592\text{pH}$$

$$\Delta G (12) = G (*) - G (*) + 0.5G (\text{H}_2) + 0.0592\text{pH}$$

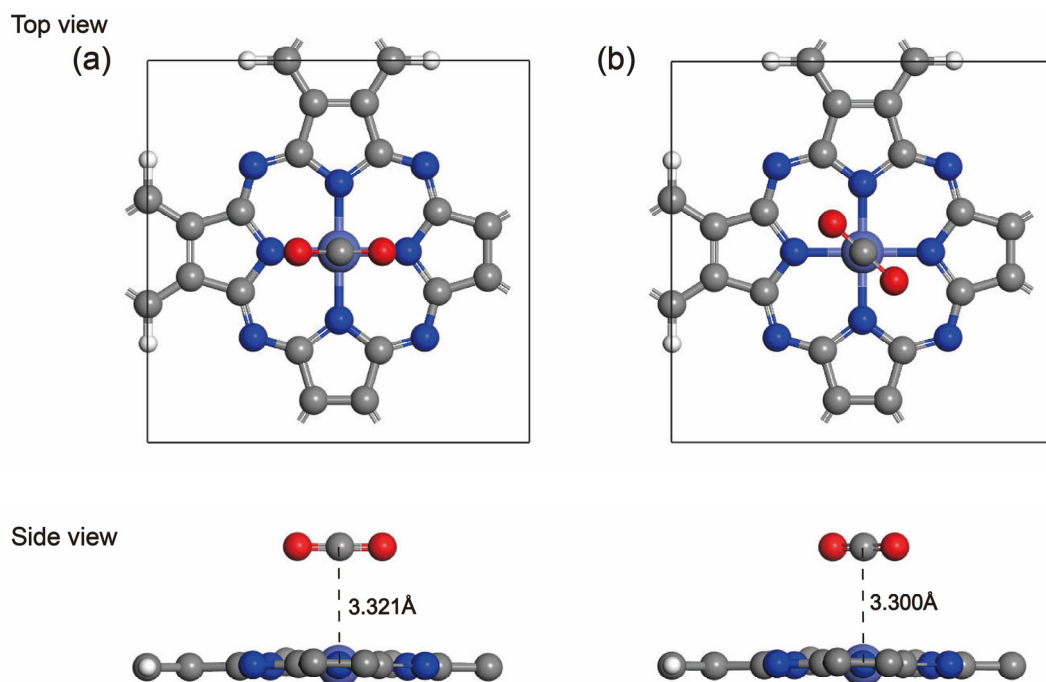


Figure S7. Two adsorption configurations of $^*\text{CO}_2$ based on CHE

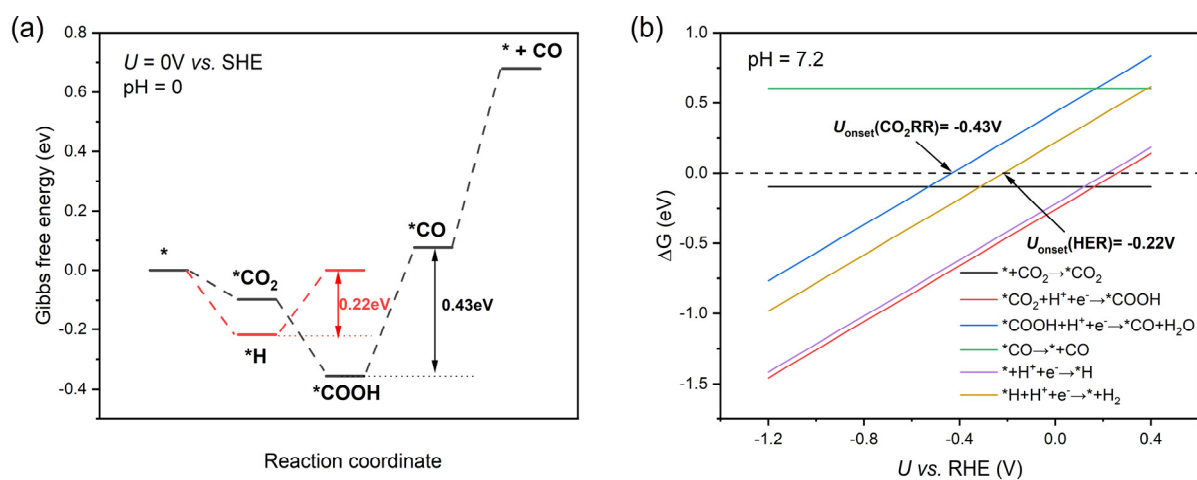


Figure S8. (a) The Gibbs free energy profiles of CO_2RR and HER along the pathways for Co-PC at $\text{pH}=0$, $U=0\text{V vs. SHE}$. The black line represents CO_2RR , and red line represents HER . (b) Potential-dependent reaction energies of all element reactions of CO_2RR and HER .

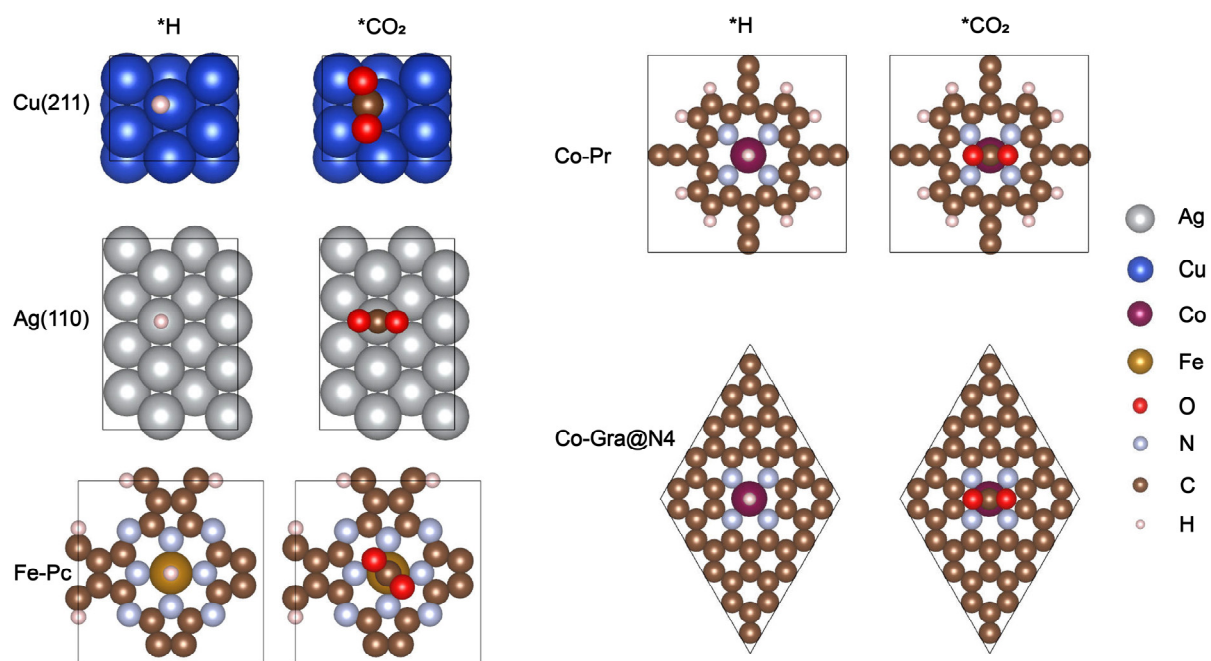


Figure S9. Top view of the optimized structures of $\ast\text{H}$, $\ast\text{CO}_2$ on Cu (211), Ag (110), Fe-Pc, Co-Pr, and Co-Gra@N4 at $U = -1.4$ V vs. SHE.

Note 8. Nonlinear changes of electron amount

$$\Delta N_e(1) = N_e(*CO_2) - N_e(*) - N_e(CO_2(aq))$$

$$\Delta N_e(2) = N_e(*COOH) + N_e(H_2O) - N_e(*CO_2) - \Omega(H_3O^+)$$

$$\Delta N_e(3) = N_e(*CO) + 2N_e(H_2O) - N_e(*COOH) - N_e(H_3O^+)$$

$$\Delta N_e(4) = N_e(*) + N_e(CO(aq)) - N_e(*CO)$$

$$\Delta N_e(5) = N_e(*H) + N_e(H_2O) - N_e(*) - N_e(H_3O^+)$$

$$\Delta N_e(6) = N_e(*) + N_e(H_2O) + N_e(H_2(aq)) - N_e(*H) - N_e(H_3O^+)$$

Table S6. The amounts of electron transfer (ΔN_e) of all element reactions at different potential

<i>U</i> vs. SHE reactions	-0.4 V	-0.6 V	-0.8 V	-1.0 V	-1.2 V	-1.4 V	-1.6 V
(1)	0.040	0.002	0.149	0.502	0.552	0.438	0.443
(2)	0.158	0.395	0.533	0.504	0.504	0.589	0.605
(3)	0.994	0.942	1.316	0.979	0.940	1.136	1.145
(4)	0.808	0.662	0.001	0.010	0.004	-0.162	-0.194
(5)	0.055	0.175	0.430	0.765	0.970	0.980	0.958
(6)	1.944	1.825	1.570	1.235	1.03	1.020	1.041

Table S7. The slopes($\partial\Delta\Omega/\partial U$) obtained by differentiating $\Delta\Omega$ (eV)- U (V) curve at different potential

<i>U</i> vs. SHE reactions	-0.4 V	-0.6 V	-0.8 V	-1.0 V	-1.2 V	-1.4 V	-1.6 V
(1)	-0.006	0.033	0.238	0.493	0.598	0.412	0.278
(2)	0.536	0.499	0.482	0.415	0.449	0.695	0.821
(3)	0.416	0.883	1.378	1.231	0.640	0.691	1.158
(4)	1.117	0.633	-0.031	-0.116	0.349	0.167	-0.384
(5)	0.035	0.227	0.491	0.733	0.951	0.963	0.926
(6)	1.960	1.866	1.564	1.230	1.079	1.014	0.974

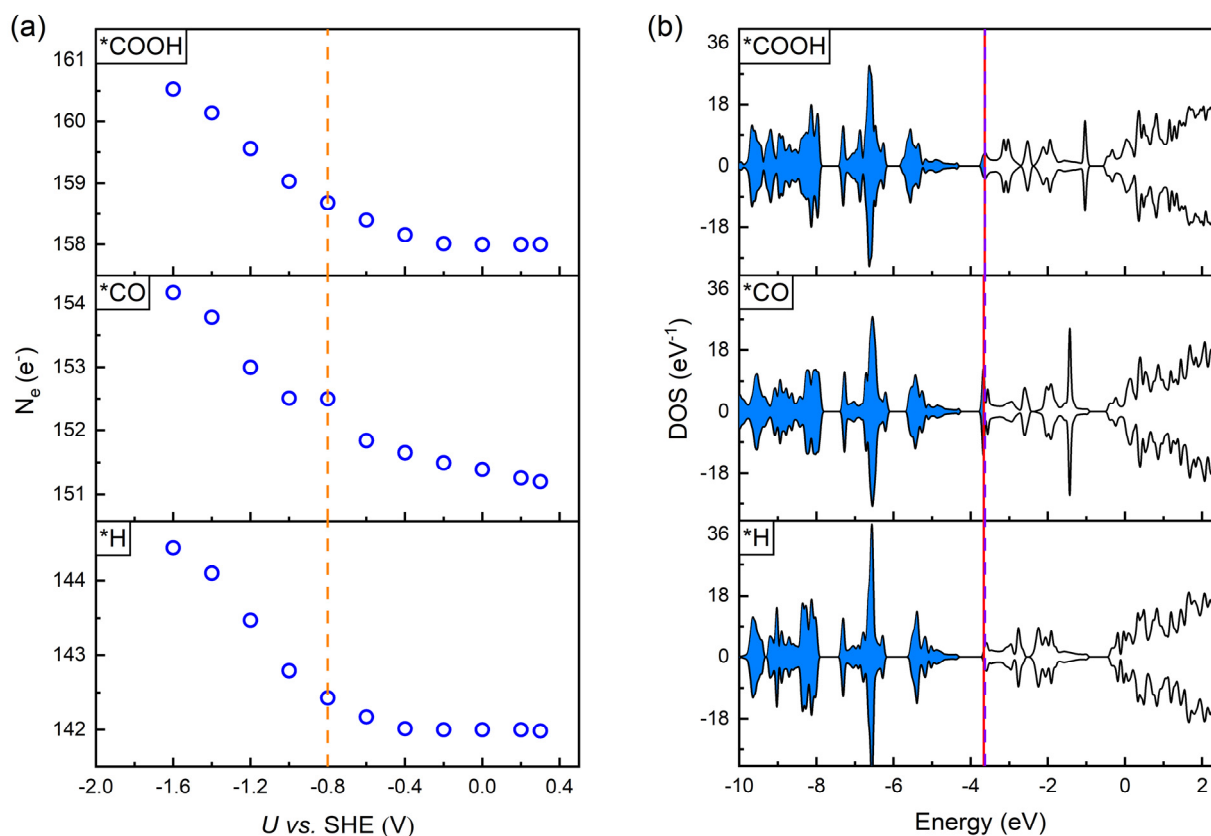


Figure S10. (a) The amount of electron of $^*\text{COOH}$, $^*\text{CO}$, and $^*\text{H}$ at different applied potential. (b) Density of states of $^*\text{COOH}$, $^*\text{CO}$, $^*\text{H}$ at $U = -0.8$ V vs. SHE. The orange dotted line denotes the amount of electron at $U = -0.8$ V vs. SHE.

References

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